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ABSTRACT

The proton spin-lattice relaxation times and Knight shifts have been measured in f.c.c. (δ-phase) and f.c.t. (ε-phase) ZrH for 1.5 \( \leq x \leq 2.0 \). Both parameters indicate that \( N(E_F) \) is very dependent upon hydrogen content with a maximum occurring at ZrH\(_{1.83}\). This behavior is ascribed to modifications in \( N(E_F) \) through a fcc-fct distortion in ZrH\(_x\) associated with a Jahn-Teller effect.

The electronic properties of the non-stoichiometric dihydrides of the IVB metals Ti, Zr, and Hf have been the subjects of numerous theoretical\(^1\text{-}^3\) and experimental\(^4\text{-}^6\) studies. Much of this interest has focused on the temperature and composition dependent fcc to fct phase transition that has been associated\(^7\text{-}^9\) with a Jahn-Teller type mechanism, as well as the more general problem of the character of the metal-hydrogen bonds.\(^1^0\text{-}^8\) Although there have been several recent nuclear magnetic resonance (NMR) studies related to the electronic structure of TiH\(_2\),\(^6\text{-}^8\) only limited NMR results\(^9\text{-}^{10}\) address the electronic properties of δ-phase (fcc) and ε-phase (fct) ZrH\(_x\). In the present work, the temperature and composition dependence of the proton spin-lattice relaxation times (\( T_1 \)) and Knight shifts (\( \delta \)) have been measured in high-purity polycrystalline ZrH\(_x\) for 1.5 \( \leq x \leq 2.0 \). These parameters, which are related\(^1\text{-}^1\) to the densities of electron
states $N(E_F)$ at the Fermi energy $E_F$, show the dominance of the core-polarization hyperfine interaction with the Zr d-electrons and yield a maximum in $N(E_F)$ near $x = 1.83$. These observations support the Jahn-Teller mechanism for the tetragonal distortion and are consistent with recent APW band-theory calculations of fcc ZrH$_2$ and photoemission spectra for ZrH$_x$.

The ZrH$_x$ samples were prepared by direct reactions between purified H$_2$ gas and zone-refined Zr foils (Materials Research Corporation - MARZ grade). The ZrH$_x$ foils were ground under an argon atmosphere to produce powders that were sealed in evacuated glass tubes. The $T_1$ values were obtained by the standard inversion-recovery method at the proton frequency of 34.5 MHz. The previously described zero-crossing method produced the $\sigma_K$ values, which are relative to an external reference of tetramethyhydroxilane, for a resonance frequency of 56.4 MHz. The $\sigma_K$ values have a precision of ±2 ppm while the exponential $T_1$ recoveries yielded $T_1$ with a precision of ±3%. The $T_1$ values were measured over the temperature range 100 K to 300 K and the $\sigma_K$ values were obtained between 170 K and 310 K, as shown in Figs. 1 and 2, respectively. There was no unusual temperature behavior for either parameter. Below 310 K, the proton $T_1$ values are assumed to be dominated by the conductive electron component $T_{1e}$ as found previously.

The composition and temperature behavior of the proton $\sigma_K$ and $(T_{1e}T)^{-1}$ parameters for ZrH$_x$ are summarized in Fig. 3 where $T$ is the absolute temperature. The major feature for $(T_{1e}T)^{-1}$ is an increase above $x = 1.65$ to reach a maximum near $x = 1.83$ before decreasing smoothly up to $x = 2.00$. $(T_{1e}T)^{-1}$ exhibits the largest temperature dependence for $1.80 < x < 1.85$ (i.e., at the peak). Similar behavior is noted for the proton $\sigma_K$ parameters; however, neither the composition nor temperature dependence of $\sigma_K$ is as large as seen for $(T_{1e}T)^{-1}$.

The proton $T_{1e}$ and $\sigma_K$ parameters are related to the electronic structure of a metal hydride through the hyperfine fields produced at the proton sites. Since the d-electron orbital terms appear to make insignificant contributions to the proton parameters in several metal hydrides, the $\sigma_K$ and $T_{1e}$ parameters can be separated as

$$\sigma_K = 2\mu_B [H_{hf}(s)N_s(E_F) + H_{hf}(d)N_d(E_F)]$$

$$\frac{1}{T_{1e}T} = 4\pi \gamma^2 H B \left\{ [H_{hf}(s)N_s(E_F)]^2 + [H_{hf}(d)N_d(E_F)]^2 \right\} q.$$  (2)

Here, $H_{hf}(s)$ and $H_{hf}(d)$ are the hyperfine fields for the Fermi contact interaction with unpaired s-electrons and transferred "core" polarization from the s-d exchange with metal d-states, respectively; $\mu_B$ is the Bohr magnetron; $\gamma$ is the proton gyromagnetic moment; $H$ is the Boltzmann's constant; and the reduction factor $q = 1/3[f(t_{2g})]^2 + 1/2[1-f(t_{2g})]^2$ in a cubic structure where $f(t_{2g})$ is the fractional
Fig. 1. Proton $T_1$ for ZrH$_x$ at $\nu_H = 34.5$ MHz.
Fig. 2. Proton Knight shifts for ZrH₆ measured by multiple-pulse zero-cross technique at 56.4 MHz.
Fig. 3. Composition dependence of proton $(T_1T)^{-1}$ and $\alpha_K$ for ZrH$_x$.

Character of the $t_{2g}$ d-orbitals at $E_F$. The $H_{hf}(s)$ is always positive, but $H_{hf}(d)$ is usually negative. Thus, although the contact and core polarization terms are additive for $(T_1T)^{-1}$, a large cancellation can occur in $\alpha_K$.

The negative proton $\alpha_K$ values in Fig. 2 clearly indicate that the core-polarization term exceeds the contact term in $\delta$-ZrH$_x$ and $\epsilon$-ZrH$_x$, which implies $N_d(E_F) > N_s(E_F)$ in these hydrides. Similar conclusions have been made for several other hydrides including $\gamma$-TiH$_x$, $\delta$-Ti$_{1-x}$V$_x$H$_x$, $\delta$-TiCuH$_x$, and $\delta$-TiCr$_2$H$_x$, hence, a relatively large $N_d(E_F)$ seems to be a general property of the hydride phases formed by group IVB metals and of at least some alloys containing Ti. A more detailed analysis of the proton $\alpha_K$ and $(T_1T)^{-1}$ values for ZrH$_x$ suggests substantial s-electron contact (or, perhaps, some orbital) contribution in $\delta$-phase ZrH$_{1.60}$ while the core-polarization seems to be the exclusive hyperfine interaction in $\epsilon$-phase ZrH$_x$. 

HYDROGEN STOICHIOMETRY, ZrH$_x$ (moles H)
The composition dependence of \((T_1, T)\) and \(\sigma_n\) in Fig. 3 is consistent with the available band theory calculations for TiH\(_2\),\(^{1,2}\) and ZrH\(_2\),\(^{3}\) as well as the Jahn-Teller mechanism\(^{2,4}\) for the fcc-fct transition. Briefly, \(N_d(E_F)\) is apparently constant in fcc \(\delta\)-ZrH\(_x\) \((x < 1.65)\) as the \(E_F\) level moves upward with \(x\), but adding more hydrogen above 1.65 causes \(E_F\) to enter the band region where \(N_d(E_F)\) increases rapidly until \(x \approx 1.83\). However, because of the electronic instability of a large \(N_d(E_F)\) the tetragonal distortion continually increases, which will tend to reduce the \(N_d(E_F)\) value as \(x\) becomes larger. The competition between \(N_d(E_F)\) increasing with more hydrogen and decreasing with the Jahn-Teller tetragonal distortion produces the \((T_1, T)\) maximum near \(x = 1.83\). This general behavior corresponds to changes seen in the photoemission spectra\(^5\) of ZrH\(_x\) as hydrogen content varies. A more detailed discussion of the electronic structure and proton parameters will be published elsewhere.

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